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THE LOWEST TRIPLET STATE FROM PMDR  
SPECTROSCOPY

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Prepared for:

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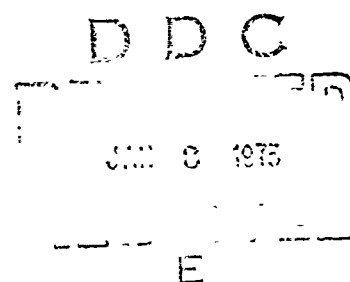
OFFICE OF NAVAL RESEARCH  
Contract No. N00014-69-A-0200-4012  
Task No. NR-056-498  
TECHNICAL REPORT NO. 15

THE MOLECULAR GEOMETRY OF PYRAZINE IN THE LOWEST  
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by

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16

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) University of California, Los Angeles M. A. El-Sayed, Principal Investigator		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP None	
3. REPORT TITLE The Molecular Geometry of Pyrazine in the Lowest Triplet State from PMDR Spectroscopy			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
5. AUTHOR(S) (First name, middle initial, last name) A. A. Gwaiz and M. A. El-Sayed			
6. REPORT DATE December 19, 1972		7a. TOTAL NO. OF PAGES 25/16	7b. NO. OF REFS 17
8a. CONTRACT OR GRANT NO. N00014-69-A-0200-4012		9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report No. 15	
b. PROJECT NO. Task No. NR-056-498		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Office of Naval Research Physics Branch Washington, D. C.	
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ABSTRACT

The triplet spin sublevel origins of the bands in the phosphorescence of pyrazine in a para-dioxane host are assigned using phosphorescence-microwave double resonance techniques. The assignments cannot be interpreted in terms of a  $D_{2h}$  structure for the molecule in the triplet state, and indicate a triplet state molecular symmetry of  $C_{2h}$  or lower.

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<sup>†</sup> This work is done in partial fulfillment of the requirements for the Ph.D. degree at UCLA.

<sup>††</sup> Contribution Number 3062

## INTRODUCTION

There have been strong indications from the structure of the absorption<sup>1,2</sup> and emission spectra that the molecular symmetry of pyrazine in the phosphorescent<sup>3</sup>  $n, \pi^*$  state is lower than  $D_{2h}$ . The instability of the  $D_{2h}$  structure in the triplet state has been interpreted<sup>3</sup> in terms of a pseudo-Jahn Teller vibronic coupling in the triplet manifold, and the appearance of multiple quanta of nontotally symmetric modes in the phosphorescence spectrum is apparently a manifestation of such vibronic coupling. The  $937\text{ cm}^{-1}$  band, assigned<sup>4</sup> as  $b_{1g}(\nu_{10a})$ , is intense and also appears in two quanta. This is believed<sup>3</sup> to be due to vibronic perturbation of  ${}^3B_{3u}(n, \pi^*)$  by  ${}^3B_{2u}(\pi, \pi^*)$  along the  $b_{1g}$  normal coordinate. The second prominent nontotally symmetric mode in the phosphorescence is the  $760\text{ cm}^{-1}$  band, assigned<sup>4</sup> as  $b_{2g}(\nu_5)$ , which also appears in two quanta, and is interpreted as arising from vibronic mixing between  ${}^3B_{3u}(n, \pi^*)$  and  ${}^3B_{1u}(\pi, \pi^*)$  via the  $b_{2g}$  mode.

The utility of phosphorescence-microwave double resonance spectroscopy<sup>5</sup> in investigating the molecular symmetry in the triplet state has been previously demonstrated in applications to benzene,<sup>6</sup> dibromonaphthalene,<sup>7</sup> tetrachlorobenzene,<sup>8</sup> and hexachlorobenzene.<sup>9</sup> The system investigated here is a  $10^{-3}\text{ M}$  solution of pyrazine in a para-dioxane host. The phosphorescence spectrum at  $1.6^\circ\text{K}$  is very sharp with an origin at  $26410\text{ cm}^{-1}$ , and two prominent nontotally symmetric vibrations displaced by  $760\text{ cm}^{-1}$  and  $937\text{ cm}^{-1}$  from the 0,0 band. The designation of the spin origins of these bands can be used to deduce the symmetry of the molecule in the triplet state. Two methods which are complementary to each other are used to determine the origins of the bands: (1) analyzing the decay curves of the bands; and (2) microwave saturation of the zero-field transitions. Microwave-induced delayed phosphorescence (MIDP) techniques<sup>10</sup> in the latter is preferable to c.w. PMDR since the signal is enhanced, and also because uncertainties as to the relative populations of the spin states are eliminated.

### EXPERIMENTAL

The experiments were performed on a solution of  $10^{-3}$  M pyrazine in para-dioxane at 1.6°K. The pyrazine, obtained from the Aldrich Chemical Company, was vacuum sublimed and the middle fraction retained. The purity of the para-dioxane (Mallinckrodt Chemical Company) appeared to be adequate, on the basis that no impurity emission was detected. The samples were flushed with helium several times and then sealed under a low helium pressure in quartz ampules. The polycrystalline sample was excited by the 3130 Å line from a high pressure mercury arc which was isolated by an aqueous solution of 0.2 grams/l  $K_2CrO_4$ , and a UG-11 glass filter. The spectrum was obtained on a Jarrell-Ash grating spectrometer with 50 slits, and the phosphorescence emission detected using an EMI-625GS photomultiplier tube. The phosphorescence decays and PMDR signals were collected on a TMC-401C CAT. The microwave source used was a Hewlett-Packard 8690B sweep oscillator with appropriate plug-ins.

### RESULTS

Three zerofield transitions were detected at microwave frequencies of 9.886, 9.584 and 0.30 GHz. The transitions may be assigned to  $|D| + |E|$ ,  $|D| - |E|$  and  $2|E|$ , respectively. The ordering of the energies of the magnetic sublevels is fairly well established, having been determined by a variety of methods, including high-field optical detection,<sup>11</sup> low-field and zero-field optical detection,<sup>12,13</sup> and low-field Zeeman studies.<sup>14</sup> These studies were unanimous in assigning the ordering:  $E(\tau_y) < E(\tau_z) < E(\tau_x)$  for the axis system where z is along the N-N axis, y is the other in-plane axis and x is normal to the plane of the molecule.

MIDP experiments reveal that depopulation of the triplet occurs predominantly through  $\tau_y$  with a rate constant  $k_y = 154 \text{ sec}^{-1}$ . The rate constants for the dark levels are  $k_x = 5 \text{ sec}^{-1}$  and  $k_z = 2.5 \text{ sec}^{-1}$ .

The decays of the 0,0, 760  $\text{cm}^{-1}$  and 930  $\text{cm}^{-1}$  bands were obtained at

1.6°K (Fig. 1). Three components could be extracted from the total decay, with lifetimes: 6 msec, 200 msec and 400 msec, in agreement with MIDP results where they were assigned to the lifetimes of  $\tau_y$ ,  $\tau_x$  and  $\tau_z$ , respectively. The decay of both the 0,0 and 760  $\text{cm}^{-1}$  bands could be resolved into three components, which indicates that they originate from all three spin levels, assuming that the spin-lattice relaxation is frozen at 1.6°K.<sup>15</sup> The 937  $\text{cm}^{-1}$  band decays primarily with the medium lifetime, with very little short or long components, and hence may be assumed to originate from  $\tau_x$  with little contribution from  $\tau_y$  and  $\tau_z$ .

Table 1 shows the signs of the MIDP signals. After an appropriate delay time (30-60 msec) between the shutting-off of the exciting light and the start of the microwave sweep,  $N_y(t) \ll N_x(t)$ ,  $N_z(t)$  (where  $N$  represents the population density of the spin level), and the sign of the microwave signal immediately indicates the spin sublevel origins of the band. From the table it may be concluded that both the 0,0 and 760  $\text{cm}^{-1}$  bands originate predominantly from  $\tau_y$ . The 937  $\text{cm}^{-1}$  band originates from both  $\tau_y$  and  $\tau_x$ . However,  $\tau_x$  contributes more to the intensity than does  $\tau_y$  since the band intensity decreases when D+E is saturated, after  $\tau_y$  is allowed to decay. The 847  $\text{cm}^{-1}$ , 1519  $\text{cm}^{-1}$  and 1861  $\text{cm}^{-1}$  bands, like the 0,0, all originate mainly from  $\tau_y$ . The results of c.w. PMDR are also shown in Table 1. It is interesting to note that the 760  $\text{cm}^{-1}$  band does have a component originating from one of the top levels. Table 2 shows the experimentally determined spin sublevel origins of some representative phosphorescence bands.

### DISCUSSION

For the axis system where  $x$  is normal to the molecular plane and  $z$  passes through the nitrogens, the spatial symmetry of the lowest triplet state in  $D_{2h}$  is  $B_{3u}$ . For this point group the 0,0 is predicted to originate from  $\tau_y$  and  $\tau_z$ . This is in conflict with the observation that the 0,0 decay

has three components. It is noteworthy that time-resolved measurements of the polarization reveal<sup>16</sup> that all three spin states of the triplet contribute to the intensity of the 0,0 band in the emission of pyrazine in durene or p-dichlorobenzene hosts. Furthermore, Hall, Leung and El-Sayed<sup>13</sup> have shown that the dark level in  $D_{2h}$  has a slightly shorter lifetime than the spin level from which emission is allowed by symmetry, but not involving one center spin-orbit coupling terms. Generally,<sup>7</sup> the  $937\text{ cm}^{-1}$  and  $760\text{ cm}^{-1}$  bands are assigned to  $b_{2g}(\nu_5)$  and  $b_{1g}(\nu_{10a})$ , respectively. Zalewski<sup>4</sup> reverses this assignment, designating the  $760\text{ cm}^{-1}$  band as  $\nu_5$  and the  $937\text{ cm}^{-1}$  band as  $\nu_{10a}$ . In  $D_{2h}$ , bands of  $b_{2g}$  symmetry are predicted to originate from a single level,  $\tau_y$ , which, assuming the first assignment to be the correct one, would be in conflict with the experimental result that the  $937\text{ cm}^{-1}$  band originates from at least two spin levels. The  $760\text{ cm}^{-1}$  band is predicted to originate from  $\tau_z$ , while the experimental results reveal that it originates predominantly from  $\tau_y$  with some contribution from  $\tau_x$ . Assuming Zalewski's assignment to be correct, the predicted origin of the  $760\text{ cm}^{-1}$  band agrees with the observed origin ( $\tau_y$ ), but the  $937\text{ cm}^{-1}$  band is expected to originate from  $\tau_z$ , in conflict with experiment. These conclusions regarding the  $937\text{ cm}^{-1}$  and  $760\text{ cm}^{-1}$  bands are valid, regardless of whether the spin-lattice relaxation is frozen, since they are not derived from the decays as in the case of the 0,0. The experimental results, therefore, cannot be adequately interpreted in terms of a  $D_{2h}$  structure. Furthermore, the symmetry reduction is not exclusively crystal field induced since the vibronic bands reflect a non- $D_{2h}$  symmetry.

A plausible distortion would be to a  $C_{2v}$  boat structure. The 0,0 in  $C_{2v}$  originates from the lower two spin levels (Table 3), again, in conflict with the experimental results based on the decay of the 0,0 band. The predicted origin of the  $937\text{ cm}^{-1}$  band agrees with experiment, only if it is assumed that Zalewski's assignment is the correct one. However, the  $C_{2v}$  structure



may be ruled out on the basis of the predicted origins of the  $760\text{ cm}^{-1}$  band which is in conflict with experiment, irrespective of whether it is assigned to  $b_1$  ( $b_{1g}$  in  $D_{2h}$ ) or  $b_2$  ( $b_{2g}$  in  $D_{2h}$ ).

The experimental results, however, do not conflict with a symmetry of  $C_{2h}$  or lower symmetry, where the bands are predicted to originate from all three spin levels.

The prominence of  $b_{1g}$  and  $b_{2g}$  vibrations is actually consistent with a  $C_{2h}$  structure. The  $760\text{ cm}^{-1}$  vibration ( $b_{1g}$ ,  $\nu_{10a}$ )<sup>17</sup> for example, involves an out-of-plane displacement of the hydrogens such that the two hydrogens on one side of the N-N axis move in the same direction but opposite to the direction in which the hydrogens on the other side of the N-N axis move. Thus strong vibronic coupling along the  $b_{1g}$  coordinate could result in a permanent distortion to  $C_{2h}$  if the crystal field is anisotropic, favoring one conformation over the other. The  $930\text{ cm}^{-1}$  vibration ( $b_{2g}$ ,  $\nu_5$ )<sup>17</sup> involves opposite displacement of the hydrogens on one side of the N-N axis such that there is a reflection plane containing the N-N axis and the axis normal to the molecular plane. Strong vibronic coupling in this case would also result in distortion to  $C_{2h}$ , although the structure in this case will not be the same as that induced by the  $b_{1g}$  vibration. Which of the two forms is more stable will obviously depend on the difference in the strength of the vibronic coupling between the  $^3B_{3u(n,\pi^*)}$  and the  $^3B_{1u(n,\pi^*)}$  or  $^3B_{2u(n,\pi^*)}$  states as well as the difference in energy between the coupled states. The role of the crystal field in stabilizing the distorted form is apparently the reason for the observed sensitivity of the zerofield transition frequencies to the host crystal field. It might also be suggested that the sensitivity of the zerofield transitions of pyrazine and pyrimidine to solvents might reflect the sensitivity of the type of the frozen geometry of the molecule as well as the difference in the energy of the coupled states to the host crystal field. Spin orbit coupling between these states could also contribute to the zerofield splittings of the  $^3B_{1u(n,\pi^*)}$  state. This contribution is also sensitive to the solvent, which determines the relative energies of these states as well as the type of distortion. This could also be an added reason for the sensitivity of the zerofield splittings of pyrimidine and pyrazine to the

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support of the Office of Naval Research.

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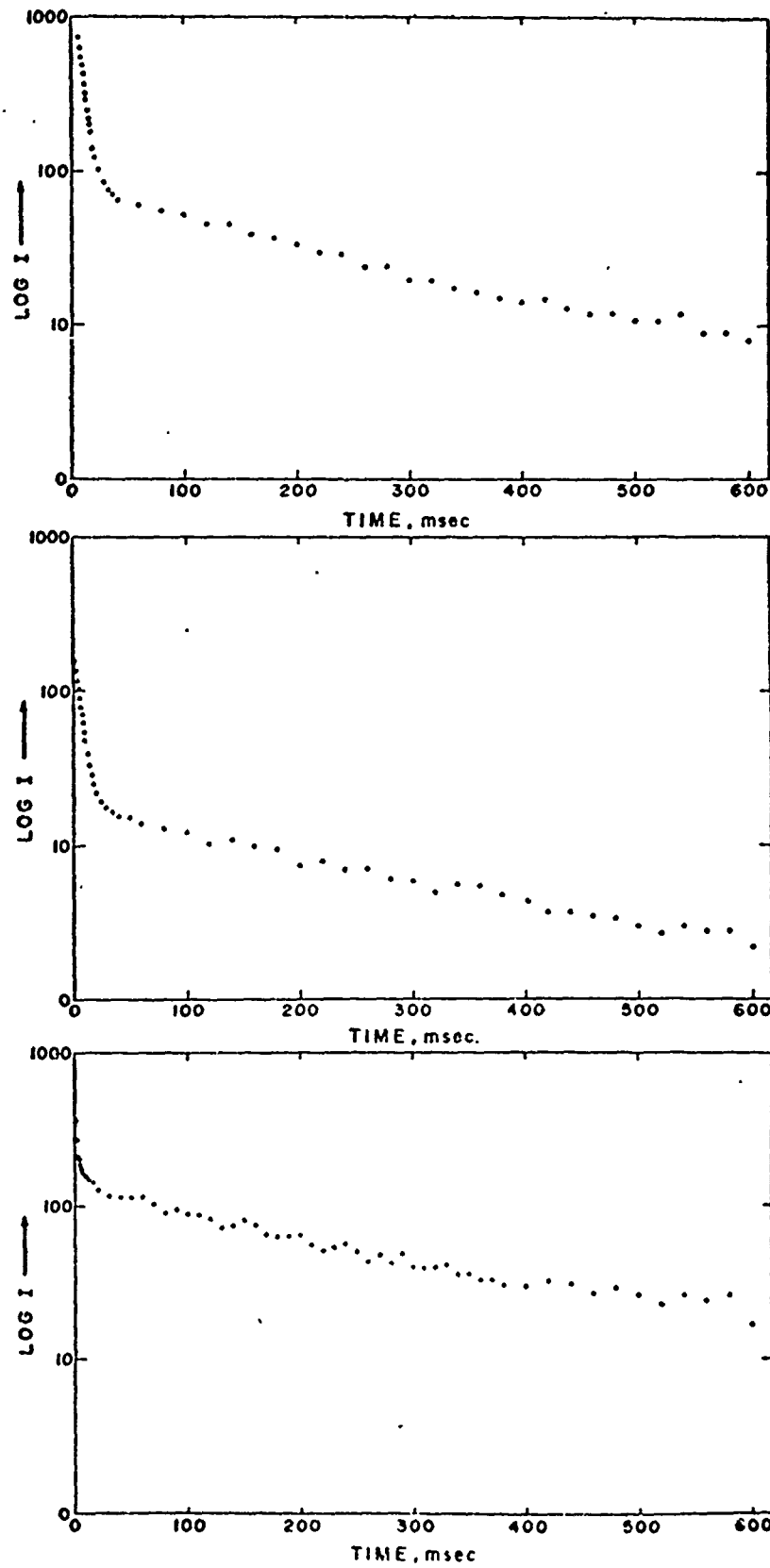
FIGURE CAPTIONS

Figure 1. The decays of the 0,0 (top),  $760\text{ cm}^{-1}$  (middle), and  $937\text{ cm}^{-1}$  (bottom) bands.

Figure 2. The  $|D| + |E|$  and  $|D| - |E|$  MIDP signals for the  $760\text{ cm}^{-1}$  (top) and  $937\text{ cm}^{-1}$  (bottom) bands. The microwave frequency is 9.4 GHz at  $t = 0$ , and the sweep rate is 1.7 Mc/sec.

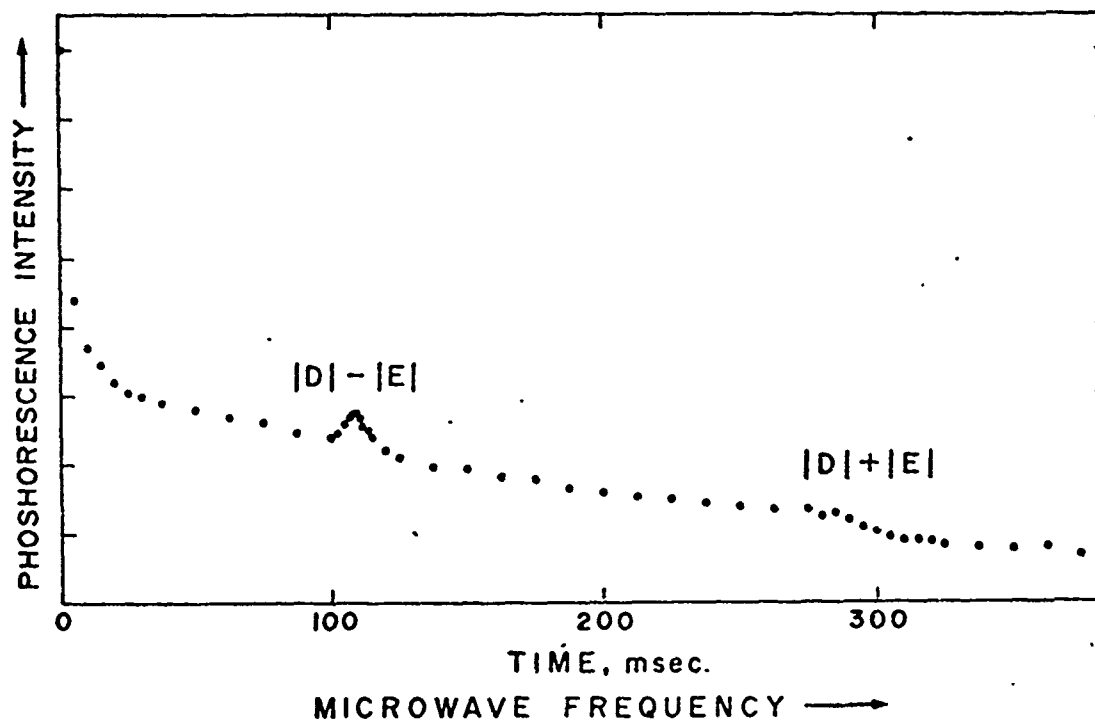
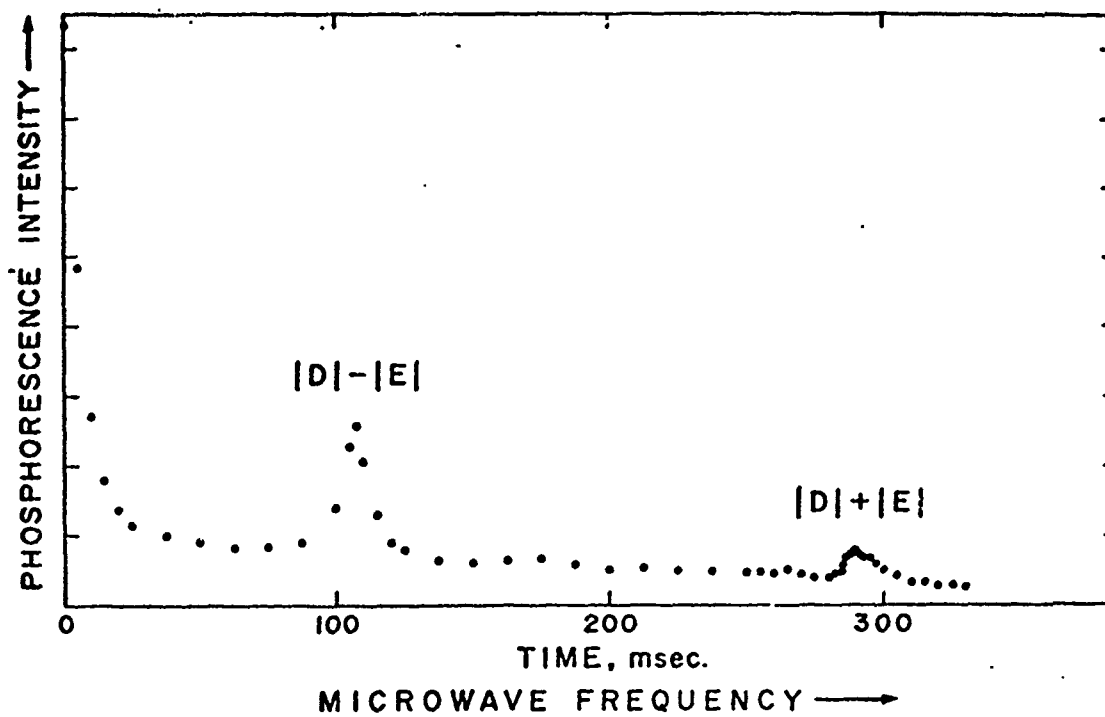
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Figure 1



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Figure 2



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TABLE 1

Signs of PMDR Signals of Representative  
Bands in the Phosphorescence of Pyrazine

$\lambda, \text{\AA}$	$\Delta\nu \text{ cm}^{-1}$	Sign of PMDR Signal			
		Chopped Excitation		C.W. Excitation	
		D + E	D - E	D - E	2E
3785.3	0	+	+	+	0
3888.4	700.3			+	0
3897.5	760.3	+	+	+	+
3910.7	846.9	+	+	0	0
3924.5	936.8	-	+	0	+
4016.3	1519.0	+	+	+	0
4018.4	1532.0			0	-
4072.1	1860.7	+	+	+	0

TABLE 2  
The Experimentally Determined Relative Contributions  
of the Spin Components to the Band Intensity

$\lambda$ (air) Å	$\nu$ (vac.) $\text{cm}^{-1}$	$\Delta\nu$ $\text{cm}^{-1}$	I (rel.)	Assignment (17)	I (rel.) of Spin Component		
					$\tau_y$	$\tau_z$	$\tau_x$
3785.3	26410.5	0	vs	0,0	s	w	w
3888.4	25710.2	700.3	vw	$\nu_4(b_{2g})$	m	w	s
3897.5	25650.2	760.3	w	$\nu_{10a}(b_{1g})$	s	w	s
3910.7	25563.6	846.9	vw	$2\nu_{16b}(2b_{3u})$	s	w	w
3924.5	25473.7	936.8	vw	$\nu_5(b_{2g})$	m	w	s
4016.3	24891.5	1519.0	m	$2\nu_{10a}(2b_{1g})$	s	w	w
4018.4	24878.5	1532.0	vw	$\nu_{8b}(b_{3g})$	w	s	w
4072.1	24549.8	1860.7	s	$2\nu_5(2b_{2g})$	s	w	w

I (rel.) = relative intensity

vs, s, m, w, vw = very strong, strong, medium, weak, very weak



TABLE 3  
Correlation of the Species and the Predicted Sublevel Origins of the Bands for  $D_{2h}$  and its Subgroups

$D_{2h}$		$C_{2v}$		$C_{2h}$		$C_s$	
Species	Origins	Species	Origins	Species	Origins	Species	Origins
$a_g$	$\tau_y, \tau_z$	$a_1$	$\tau_y, \tau_z$	$a_g$	$\tau_x, \tau_y, \tau_z$	$a'$	$\tau_x, \tau_y, \tau_z$
$b_{1g}$	$\tau_z$	$b_1$	$\tau_y, \tau_x$	$b_g$	$\tau_x, \tau_y, \tau_z$	$a''$	$\tau_x, \tau_y, \tau_z$
$b_{2g}$	$\tau_y$	$b_2$	$\tau_z, \tau_x$	$a_g$	$\tau_x, \tau_y, \tau_z$	$a''$	$\tau_x, \tau_y, \tau_z$